Effects of Lactic and Citric Acid on Early-age Engineering Properties of Portland / Calcium Aluminate Blended Cements

Gediminas Kastiukas[1], Xiangming Zhou[1,*], João Castro-Gomes[2], Shifeng Huang[3], Mohamed Saafi[4]

[1*]Department of Mechanical, Aerospace and Civil Engineering, Brunel University
Uxbridge, Middlesex UB8 3PH, United Kingdom
e-mail: <Xiangming.Zhou@brunel.ac.uk>

[2]C-MADE, Centre of Materials and Building Technology, Department of Civil Engineering and Architecture, University of Beira Interior, Covilhã, Portugal

[3]Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Ji'nan, China

[4]Department of Engineering, Lancaster University, Bailrigg, Lancaster LA1 4YR, United Kingdom

Abstract: In this study, Portland / Calcium Aluminate blended cement (PC/CAC) was combined with citric acid or lactic acid as additives to investigate the effects of the aforementioned carboxylic acids on the hydration reactions of PC/CAC as a potential fast hardening and low cost repair material for concrete. Mortar specimens with the carboxylic acid additives of either 0.5, 1 or 3% by weight, prepared with a binder:sand:water ratio (by weight) of 1:3:0.5, were subjected to flexural and compressive strength tests at early ages up to 28 days. In order to understand the phase composition of the hydrates in the PC/CAC systems, XRD analyses were conducted on ground PC/CAC mortars with and without carboxylic acid at 7, 14 and 28 days. In combination with this, SEM images of selected mortar specimens were also taken at the same times for visual analyses of hydrates. Citric acid did not have any beneficial effect on enhancing the calcium silicate phase as initially assumed and instead reduced the strength of PC/CAC cement at all levels of concentration. The experiment analyses revealed that Portlandite crystals were the major hydrate phase in PC/CAC with lactic and citric acids. Lactic acid below 2% wt. improved both compressive and flexural strength gained at early ages due to improved crystallinity of the calcium hydroxide crystals. Combined with its inherent rapid setting time, PC/CAC blended cements have a potential to be developed into a suitable repair material for concrete.

Keywords: Admixture; Calcium Aluminate Cement (CAC); Citric acid; Early-age engineering property; Hydration; Lactic acid; PC/CAC blended cement; Portlandite crystal

1 Introduction

1.1 PC/CAC based mortar

Repair technology has become increasingly important in modern construction practice. Demands for repair and protection of existing concrete infrastructure have dramatically increased in the last few decades which are consistent with greater appreciation of sustainability. A quality repair material often requires rapid setting and hardening, good adhesion, compatibility with existing concrete, dimensional stability, and corrosion resistance. Calcium aluminate cement (CAC) has the potential to meet these repair requirements[1].

CAC has proven high strength development which is usually attributed to the formation of $2CAH_8$, $3CAH_6$ and CAH_{10} [2], [3]. CAC was developed during the last decade of the nineteenth century as an alternative to Portland cement (PC) to prevent structural concrete elements from serious sulphate attack. Other major fields of CAC application are in refractory concrete for industrial use in processes involving high temperatures [4] and in so-called ‘building chemistry’ where it constitutes one part of a complex mixture of mineral and organic ingredients for applications such as self-levelling screeds and tile cement [5]. CAC distinguishes itself from PC by containing a much higher concentration of alumina, normally 30-90% by weight [6]. Besides, CAC is also considered as a type of sustainable cement since CAC clinker contains less calcium compounds than PC clinker. In this case, less limestone is used in the manufacturing of CAC clinker, thus reducing the CO_2 emissions derived from the raw materials compared with PC clinker production [7]. CAC clinker is comprised of the same basic oxides as PC clinker such as lime, silica, alumina, and iron oxide, however the proportions of oxides are fairly different in CAC and PC clinkers. All CACs contain mono-calcium aluminate (CA or $CaAl_2O_4$) as the main hydraulic phase. Other phases may be present based on the type of CAC however it is important to note that C_3A is not a normal component of CACs [2].

Advanced material research has recently focused on ettringite rich cement compounds [8] which are known to be a dominant formation in CAC. Some properties including the hydration inhibition phenomena in these ettringite rich materials from PC/CAC/C$ (where C$ represents Calcium Sulphate (CS) systems), have been recently evaluated [9][10][11] and are of key importance to the engineering community as a more advanced appreciation on the mechanisms needs to be developed. CAC's have several unique properties which could make them the materials of choice in concrete repair applications. When CAC is used alone as a conventional mortar, these properties include: 1. rapid hardening, even at low temperatures; 2. high temperature resistance/refractory performance; 3. resistance to a wide range of chemically aggressive conditions; and 4. resistance to impact and abrasion [6][12][13][14]. Cementitious products based on ettringite have a broad range of uses: formulations with water contents near the minimum requirement to ensure plasticity are widely used in proprietary floor screeds, high performance tile grouts, refractory kiln and sewage lining.

However the use of PC/CAC based systems as a repair material is not considered as often as polymer-modified cementitious mortars which are traditionally strong candidates for repair materials. One reason for this is that the annual production of CAC is very small, around 1 per cent of PC in the UK market. Fondu, the brand of CAC used in this study and produced by Kerneos Ltd, is 3 to 4 times more expensive than PC, while white CAC is 10 times more expensive. This is governed by the cost of alumina derived from the natural mineral bauxite which is also primarily used in aluminium production, making it much more valuable than limestone used for PC production. Due to the high market price of CAC, it has not been economical and hence unpopular to use it alone for larger scale repairs. For this reason, research has led us to investigate its use as a replacement in minor quantities in PC for some desirable applications. If CAC is able to impart its attractive rapid hardening properties to PC, it would make for a very useful repair material with relatively low cost compared with pure CAC-based repair material. Due to its rapid setting, a PC/CAC system could be utilized in rapid repair of PC structures, such as highways, airport runways, and bridge decks. It could reduce the waiting time and cost associated with ordinary PC repair materials. Periods of sustained interruption for example in a busy highway, airport runway, bridge, etc., will cause significant economic loss. By using PC/CAC materials, the potential to reduce interruption to services could be greatly reduced, therefore allowing valuable time and resources to be saved.

The efficient repair and replacement of concrete often requires a rapid setting material that can be placed and cured in a relatively short period of time. Frequently, temporary repairs are made using materials that are later found to be incompatible with the existing pavement, structure, and environment. This practice causes these materials to fail prematurely, frequently requiring re-repair [15]. However research shows that PC/CAC based mortars may attain lower compressive strength resistance than PC mortar [16][17]. Mortar based on this binary system drops in compressive and flexural strength with increased concentrations of CAC[11] [16]. Previously, the main areas of research involving CAC in binary and tertiary systems have been related to optimizing setting time, mechanical strength, and fracture toughness [4][18][19], [20]. To the best of the authors’ knowledge, research on the combination of PC/CAC blends with chemical admixtures of organic and inorganic nature has not been investigated, allowing this study to create the opening in this field of research.

1.2 Lactic and citric acid addition

Lactic and citric acid are organic admixtures which belong to the carboxylic group of acids. Citric acid has been found to be one of the more effective acids at retarding PC hydration through the adsorption of citrate ions onto the surface of the Portland cement grain surface [21]. Ions of calcium, alumina, silica and iron are all potentially capable of chelating with organic compounds. In practice, the most widely used retarders are chiefly hydroxyl carboxylic acids or their salts [22][23]. Other studies on the interaction of citric acid with calcium sulphate hemihydrate, i.e. $CaSO_4 \cdot 1/2H_2O$, confirm that the kinetics of hydration and setting time were governed by adsorption of the acids on the surface of the gypsum crystals and reduced interlocking of the microstructure [24]. The addition of citric acid to calcium sulphoaluminate cement increased the setting time, modified the morphology of the ettringite, changed the microstructural configuration and prevented a decrease in compressive strength by delayed ettringite formation[25].

Further investigations have been aimed to understand the mechanisms of the retardation using citric acid. Pore solutions, collected after different times of hydration, have been analysed for ion concentrations and organic carbon. The zeta potential as well as the composition of the hydrated solid phases has been studied [25][26]. Singh et al. [21] found that the zeta potential of cement decreases with increasing additions of citric acid, which was explained by the adsorption of citrate ions onto the positively charged surfaces of the Portland cement grains. Schwarz [26] concluded that citrate ions increase the dissolution rate of the ferrite phase. In the presence of PC/CAC cement, it was found to have a beneficial effect on strength development and appeared to reduce the retardation of the silicate phase hydration [11]. On the contrary, lactic acid has been shown to accelerate the hydration of Portland cement as proved by electrical conductivity measurements indicating that lactic acid formed a salt of calcium lactate during the interaction with Portlandite [30]. This product would also be beneficial in PC/CAC systems.

The main objective of this study was to investigate and evaluate the effects of the addition of lactic acid and citric acid on the compressive and flexural strength development of ternary PC/CAC/CS blends focusing particularly on the microstructure development and hydration products. The intention is also to develop a mortar with high early ettringite precipitation through the addition of lactic acid and reduce the disruption to the hydration of the silicate phases which contribute to the long term strength through the addition of citric acid. For this purpose mortar specimens were prepared using six PC/ CAC/CS blends of varying citric and lactic acid additions to determine the compressive and flexural strengths up to 28 days. Experimental techniques such as SEM/BEI/EDX and XRD were employed to understand the mechanism of hydration of the ternary mortar at different ages.

2 Experimental Program

2.1 Materials and specimen preparation

The weight percentages of the cementitious materials in the mortar formulations are summarized in Table 3. The additional dose of 5% calcium sulphate anhydrite and 1% hydrated lime (HL) were used as part of the base mix due to these two parameters having the greatest influence on the increased precipitation of ettringite. Samples with 0.5,1 and 3% by weight lactic acid are named L05, L1 and L3, respectively. Samples with 0.5,1 and 3% citric acid are named C05, C1 and C3, respectively.

The raw materials used for the preparation of the 9 different mortar mixes in this study were CEM I 42.5 R Portland cement (PC) obtained from *Castle Cement Limited* and CAC cement (CAC) from *Kerneos Ltd*; the chemical composition determined by SEM-EDS and physical properties can be seen in Table 1 and in Table 2, respectively. In both cases, relevant EN Standards were met. CEN standard sand and distilled water were employed for preparing mortar mixes. ACS reagent grade CS ($CaSO_4$), HL ($Ca(OH)_2$), lactic acid ($CH_3CH(OH)COOH$) and citric acid ($(HOC(COOH)(CH_2COOH)_2$, all purchased from *Sigma-Aldrich*, were used as the additives. All samples with HL and lactic acid or citric acid additives had a total cementitious materials ratio of 74:20:5:1 (i.e. PC:CAC:CS:HL) by weight to assess the influence of lactic acid and citric acid on these mixtures. Trial mixes were carried out prior to commencement of work to ensure that the mix design and material combinations met the requirements of the specification and method of use. The total cementitious materials: sand: water ratio of 1:3:0.5 by weight set by EN 196-1 for determining strength of cement was adopted. The 40x40x160mm^3 mortar prism specimens were prepared using a bench-top mortar mixer conforming to EN 196-1 and mechanically compacted in two layers.

Table 1

Chemical composition of PC and CAC determined by SEM-EDS (% by weight)

	CaO	Fe_2O_3	Al_2O_3	SiO_2	MgO	TiO_2	K_2O
PC	71.45	3.10	4.98	18.31	1.15	0	1.01
CAC	42.06	17.04	35.54	3.43	0	1.93	0

Table 2

Physical properties of the cements (PC & CAC) used in this study

	Blaine fineness (cm2/g)	Bulk density (kg/m3)
PC	4200	587
CAC	6030	1100

Immediately after casting and surface preparation**,** the specimens were covered with 0.2mm-thick polyethylene sheets to stop moisture loss and cured in a laboratory environment at approximately 20°C.. The specimens were demoulded after 24h and then moved into a humidity chamber to continue curing at the environment of 20±1°C and relative humidity 95±5% until the designated testing age.

Table 3

Weight percentages of cementitious materials in mortar formulations (% by weight)

Mix ID	PC	CAC	CS Calcium Sulphate anhydrite	HL Hydrated lime	LA Lactic acid	CA Citric acid
R1	80	20	-	-	-	-
R2	75	20	5	-	-	-
R3	74	20	5	1	-	-
C05	74	20	5	1	-	0.5
C1	74	20	5	1	-	1
C3	74	20	5	1	-	3
L05	74	20	5	1	0.5	-
L1	74	20	5	1	1	-
L3	74	20	5	1	3	-

2.2 Flexural Strength

All specimens were taken directly from the curing chamber and tested under controlled laboratory conditions. Three specimens at each specified age and each lactic or citric acid content were broken in bending using a three-point bending test conforming to EN 196-1 using an Instron universal testing machine. By doing so, flexural strength of various mixtures was obtained.

2.3 Compressive Strength

Six specimens, each a broken half from a flexural test, were tested under uniaxial compression conforming to EN 196-1 for compressive strength under the same laboratory conditions applied in the flexural strength test. The crushing load was also determined using the same Instron universal testing machine.

2.4 Scanning Electron Microscope (SEM)

SEM sample preparation was done through the removal of free water from hydrated cement by solvent exchange. After drying, the samples were stored in air-tight plastic cups in a desiccator containing silica gel to create a dry and CO_2-free environment. For the microscopical investigations, pieces of the samples were collected after testing for strength and immediately immersed in ethanol for 24 h to stop hydration and then subsequently dried at 40 °C for 24 h. Following this, they were impregnated using a low viscosity epoxy and polished down to 0.3 μm using an EcoMet 250 grinder-polisher. A SC7640 high resolution sputter coater was then used to coat the samples with approximately 12nm of gold film to give the specimen surface better conductivity. The coated samples were then examined using a Zeiss Supra 35VP scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectroscopy (EDX) analyser from EDAX. The EDX point analyses were used to determine the elemental compositions of the hydrate products. The analyses were carried out using an accelerate voltage of 20 kV to ensure a good compromise between spatial resolution and adequate excitation. Over 10 points (EDX spots) per sample were analysed.

2.5 X-ray Diffraction (XRD)

Selected samples were analysed by XRD to investigate the effect of lactic and citric acid dose on the cured PC/CAC mortar. The specimens were gently ground using a mortar pestle and the mineral phases identified by Cu-K(α) radiation using a Bruker D8 Advance diffractometer for powder analysis at 40 kV, 30mA. The powder sample was mounted in a back loading sample holder and diffraction patterns were evaluated with DIFFRAC SUITE software and powder diffraction database (PDF2 ICCD 2000).

3 Results and Discussion

The compressive and flexural strength results of the mortars are given in Figures 1-4. SEM images and diffraction patterns of selected mixes are shown in Figures 5-7 and 8-10, respectively.

3.1 Compressive and flexural strength

The results of the compression test of investigated mortars are summarized in Figures 1-4. It can be seen, for sample C3 containing 3% by wt. citric acid, at 7 days the compressive and flexural strength reduced to 6.22% and 26.85% of the initial value (the values of R3 samples without citric acid), respectively (see Figures 1 and 2). The reductions in strength at this particular age and all other ages clearly indicate that addition of citric acid impedes the hydration process. Although this effect on strength is apparent and is observed at all curing ages, the difference in compressive and flexural strength is less severe at 14 days. The compressive and flexural strength of mixture C05 containing 0.5% by wt. citric acid reached 26.6MPa and 5.56MPa, respectively. The dissolution of alite (C_3S) and aluminate slows down considerably in the presence of citric acid therefore affecting the formation of the different hydration products. However this effect has a short duration since all of the citric acid gets removed from the pore solution in the early stages of hydration [27].

This may explain why the inhibiting effect of citric acid is less severe on the mechanical strength at 14 and 28 days. Also from Fig. 1 it is interesting to observe that there was no change in compressive strength from 7 to 14 days in the sample C1 but a subsequent steep increase in 28 day strength. The strength enhancement may be attributed to a modification of the microstructures in the presence of the citric acid, which resulted in denser matrices of reaction products and has been reported in similar work done on the behaviour of calcium sulphoaluminate cement with citric acid [25]. The opposite relationship is observed in the sample C05 which demonstrated an increase in compressive and flexural strength from 7 to 14 days but a reduction from 14 to 28 days. Sample C3 exhibits the same but more subtle change in compressive and flexural strength. It is observed that the mechanical strength of PC/CAC binders with additions of citric acid other than at 1% wt. contributed to a reduction in strength from 14 to 28 days. In addition, all samples made with citric acid attained flexural strengths well below the reference mortar R3 as shown in Figure. 2.

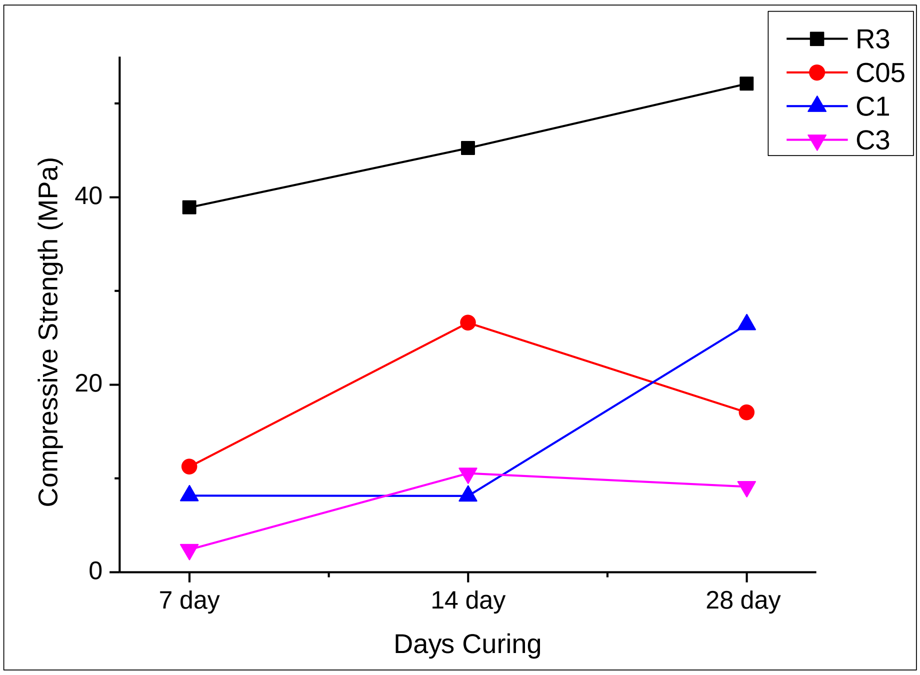


Figure 1 Influence of citric acid on compressive strength of mortar samples

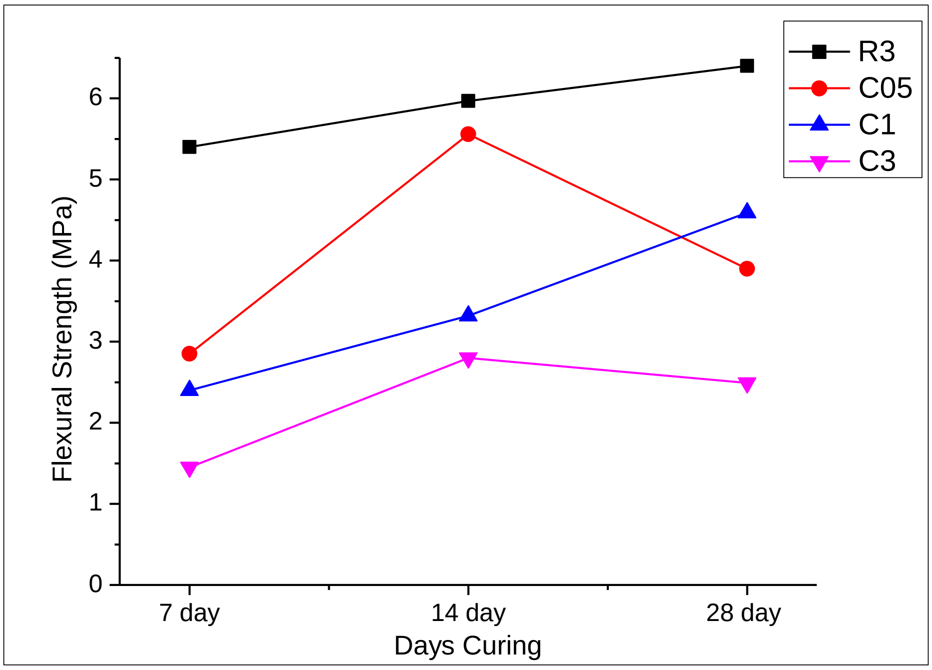


Figure 2 Influence of citric acid on flexural strength of mortar samples

At concentration of 0.5 and 1% wt., lactic acid was able to improve the compressive strength at ages 7 and 14 days, although eventually reaching the same 28 day strength as the reference mix R3 without lactic acid (see Figure 3). This behaviour may be attributed to the higher crystallinity of the calcium hydroxide crystals. The improved crystallinity of the calcium hydroxide crystals can be seen in the SEM image taken of mix L1 with 1% wt. lactic acid shown in Figure.5 (a). However an increase to a 3% wt. dose of lactic acid reduces the compressive strength to below that of the reference mortar R3. Although previous studies have shown that an increase in lactic acid of up to 20% wt. at a water/solids ratio of 0.5 increased the initial and final setting time of PC, they have not reported any improvement to strength [31]. Perhaps a saturation limit exists after which the lactic acid produces a hydrate which does not beneficially contribute to the strength. Another possibility is that the lactic acid no longer enhances the precipitation of hydrates but instead blocks it, a phenomenon exhibited by other carboxylic acids such as malic acid [22]. The flexural strength of mortars with additions of lactic acid remain relatively unchanged throughout the 28 day curing and did not surpass the flexural strength of the reference mix R3 except for the samples L05 at 7 and 14 days (see Figure 4).

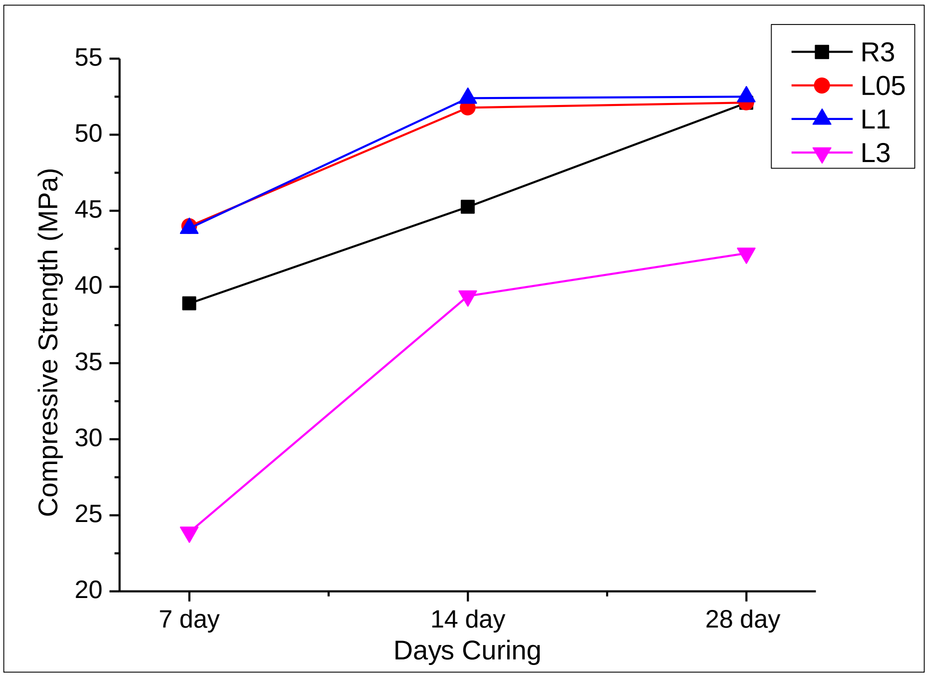


Figure 4 Influence of lactic acid on compressive strength of mortar samples

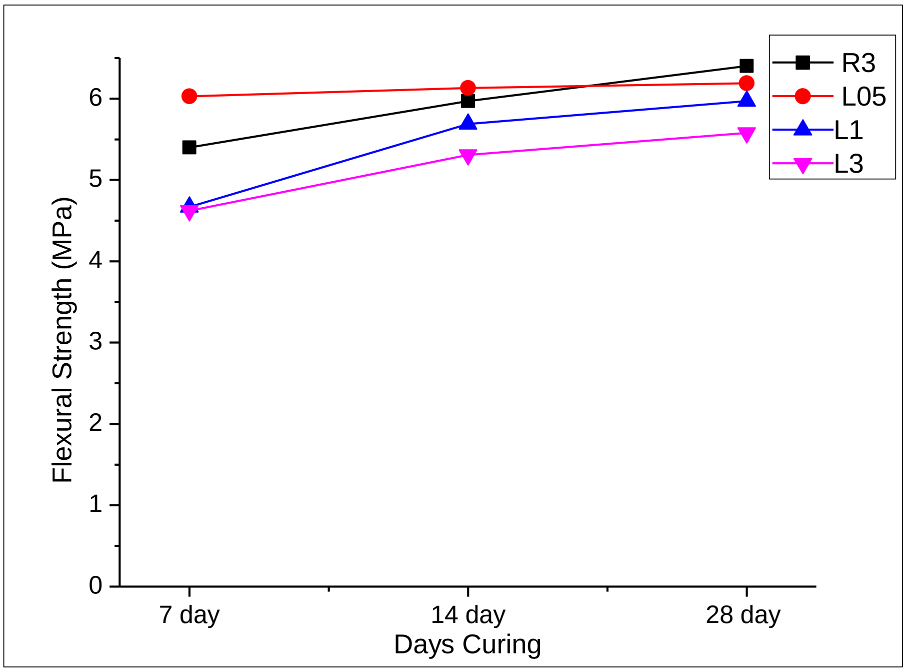
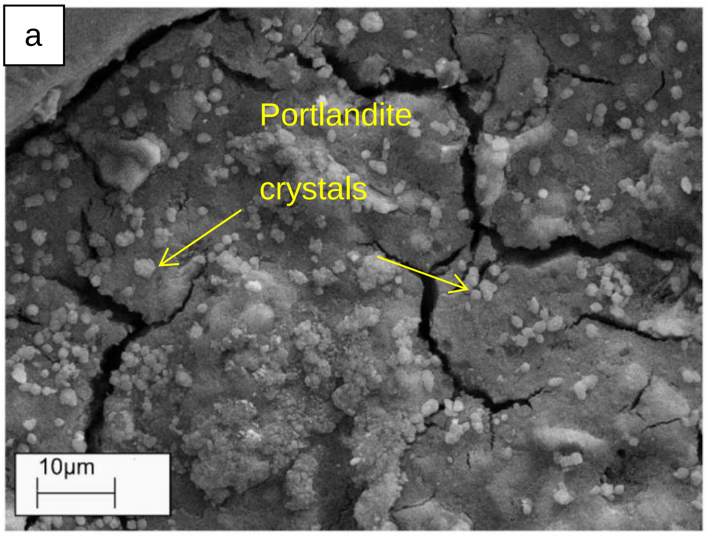
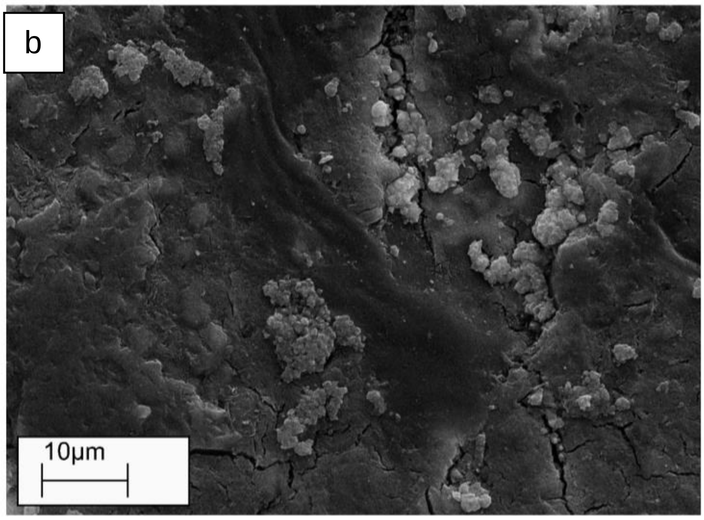


Figure 3 Influence of lactic acid on flexural strength of mortar samples

3.2 Morphology

It can be clearly seen the portlandite crystals which have formed in the R3 mix at 28 days shown in Fig. 5(a). The CH crystals have grown in large concentrated masses in the form of clusters rather than finely dispersed particles of complex and irregular shapes. Fig. 5(a) shows sample L1 containing 1% wt. lactic acid with larger portlandite crystal formations which have grown on existing clusters rather than precipitating new crystals in the microstructure. When increasing the addition of LA to 3% by weight in sample L3, the Portlandite crystals fail to form as shown by Fig. 5(c). Calcium lactate salts were not observed in any of the samples with lactic acid addition, contrary to what previous studies have shown [27]. These results are consistent with the mechanical results presented in Figures. 3 and 4 which show the sample L3 reaching lower compressive and flexural strengths respectively. In a previous study using malic acid [23], a carboxylic acid from the same group as citric acid and lactic acid, it was shown that very little Portlandite is also formed, indicating a strong retardation of hydration in PC. This trend increased with higher concentrations of malic acid. The probable cause for this, as pointed out by Rai et al. [22], may be that during hydration, Portlandite can react with lactic acid evolving heat of neutralisation causing the Portlandite to disappear. Furthermore the SEM image of L3 in Figure 5(c) shows the mortar matrix without Portlandite crystals supporting the idea that too high a dose of (>1.0%) of lactic acid obstructs the hydration of Portlandite. An addition of lactic acid above 1% can be assumed to be detrimental to the formation of portlandite crystals in PC/CAC cement binders.


a
Portlandite
crystals
10µm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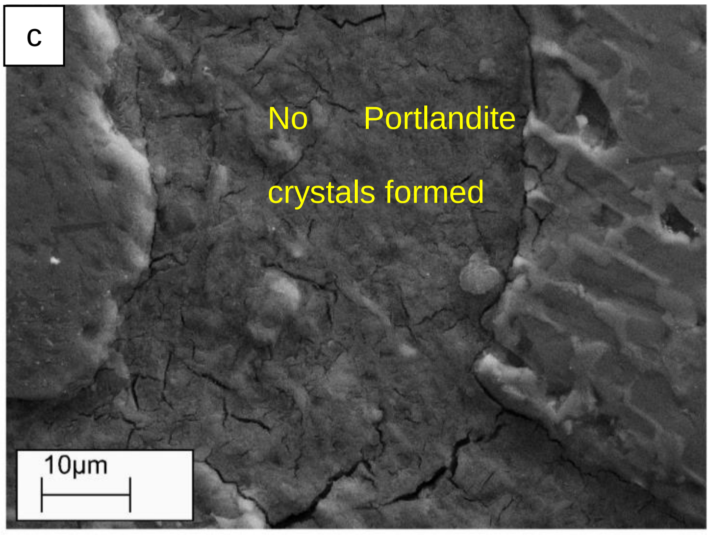

Figure 5: SEM images of (a) mix R3 (without LA) at 28 days x5k (b) mix L1 (with 1% LA) at 28 days 5k (c) mix L3 (with 3% LA) at 28 days x5k

Figure. 6 shows SEM image of the mix L1 at 28 days at a magnification of 16k in which the only hydrates visible are the Portlandite crystals with no appearance of calcium silicate hydrate. The crystal formations in sample L1 appear larger in size and more defined than for the reference sample R3 without the addition of lactic acid.

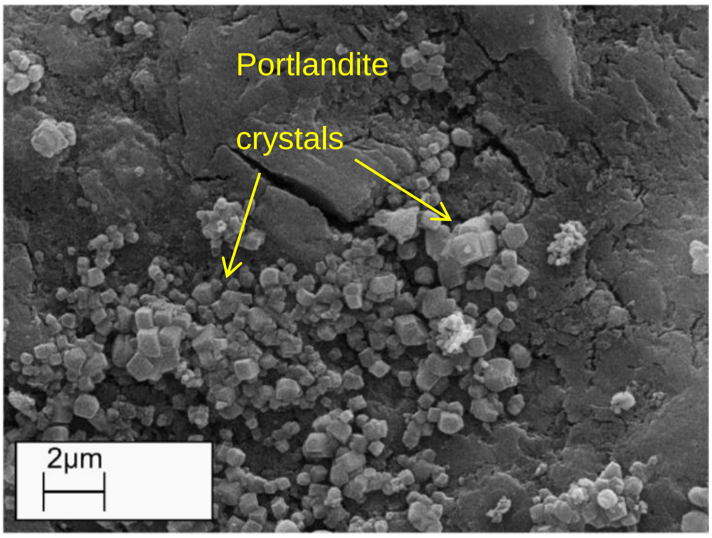

Figure 6: SEM images of mix L1 at 28 days x16k

Figure 7(a) and (b) shows backscattered images of sample C3 and L1 at 28 days respectively. It can be observed that a large quantity of unhydrated cement grains still remains present in the mortar matrix for sample C3; far more than in sample L1. Not only did the citric acid in larger quantities reduce the amount of strength inducing hydrates, but it also blocked the dissolution of existing cement grains. These observations support the strength results reported in Figures. 5-7 which indicate the L1 sample achieved in general higher flexural and compressive strength than the C3 sample and support the findings that the C3 sample reached compressive and flexural strengths far lower than the reference mix R3 and samples containing lactic acid.

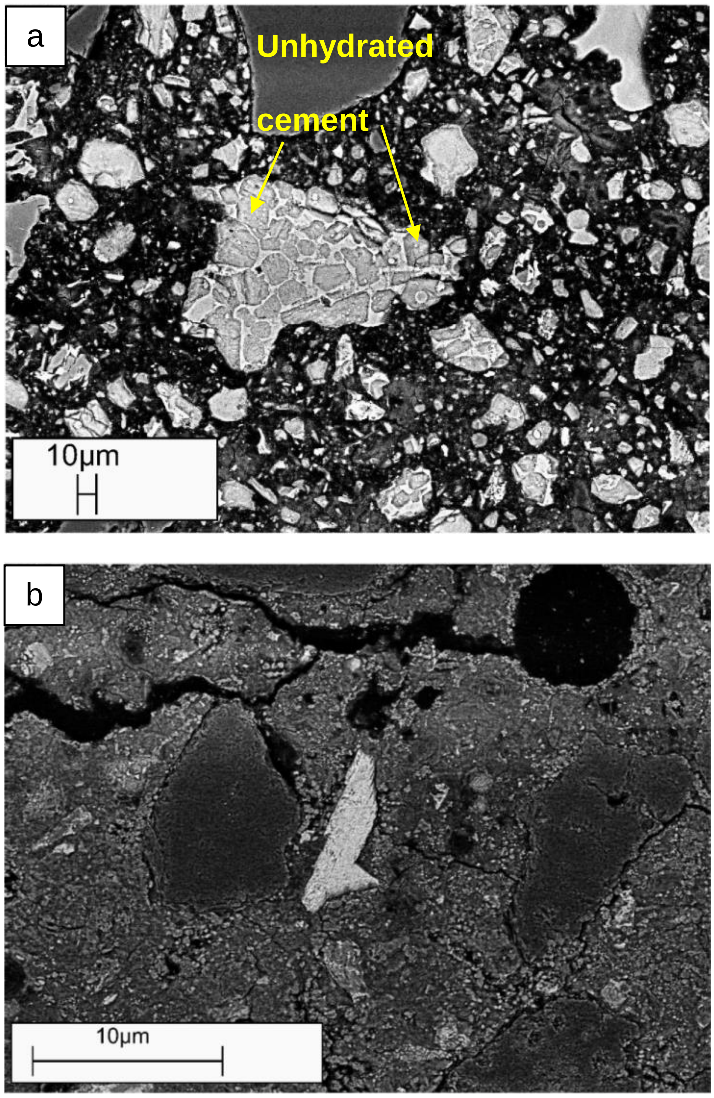

Figure 7: (a) BS image of mix C3 at 28 days x1k (b) BS image of mix L1 at 28 days x1k

3.3 X-ray diffraction

Figure. 8 shows the diffraction patterns of R3, L1 and L3 samples with doses of 0, 1 and 3% lactic acid respectively. The main crystalline product found in all samples was portlandite. Ettringite hydrate phase was also detected but in less pronounced intensity. However after 28 days the intensity of the ettringite peaks decreased, indicating that its formation reversed after the cement had hardened.

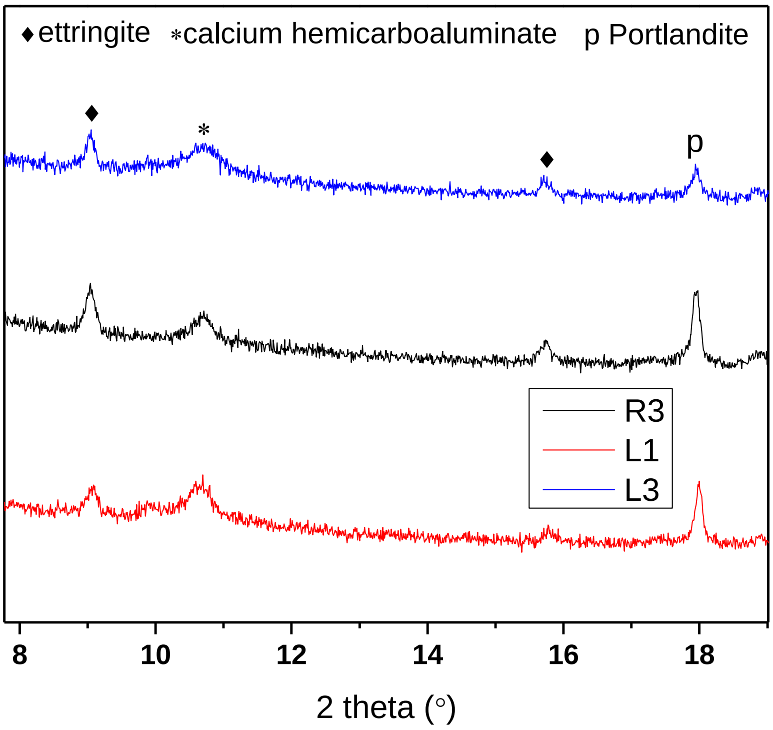

Figure 8: X ray diffraction spectrum comparing mixes R3, L1 and L3 at 28 days.

The quantity of calcium sulphate added to the mortar mix influences the quantity of the main hydrate phases ettringite and monosulphate that are produced so by increasing amounts of calcium sulphate, more ettringite is formed [29]. No significant trace of C-S-H was found in the reference sample and the addition of lactic acid did not prove successful in improving this. This is the main reason why no significant strength increase was measured relative to the reference mix R3 as shown in strength results section. Möschner et al. [30] also observed that the formation of C-

S-H was retarded in the presence of citric acid and attributed this with the retardation in the dissolution of C_3S in the presence of citric acid.

The amount of portlandite also reduced in mix L3 which can explain the reduction in mechanical strength. Portlandite seemed to be the major hydrate providing strength in PC/CAC cement mortar. To explain why C-S-H did not form, interactions between the different phases would have to be further examined. The diffraction patterns were dominated by the peaks at 10.75° 2Θ degrees, attributed to calcium hemicarboaluminate. These phases had formed when the samples were exposed to CO_2 during sample preparation for the XRD analysis and most likely formed via carbonation of the C_4AH_{19} [31] despite active efforts to exclude the exposure of samples to CO_2. Figure. 9 shows the diffraction pattern for R3, C05 and C1 corresponding to samples with doses of 0, 0.5 and 1% citric acid. Mixes with increased citric acid reduced in the quantity of ettringite but showed an increase in portlandite crystal formation.

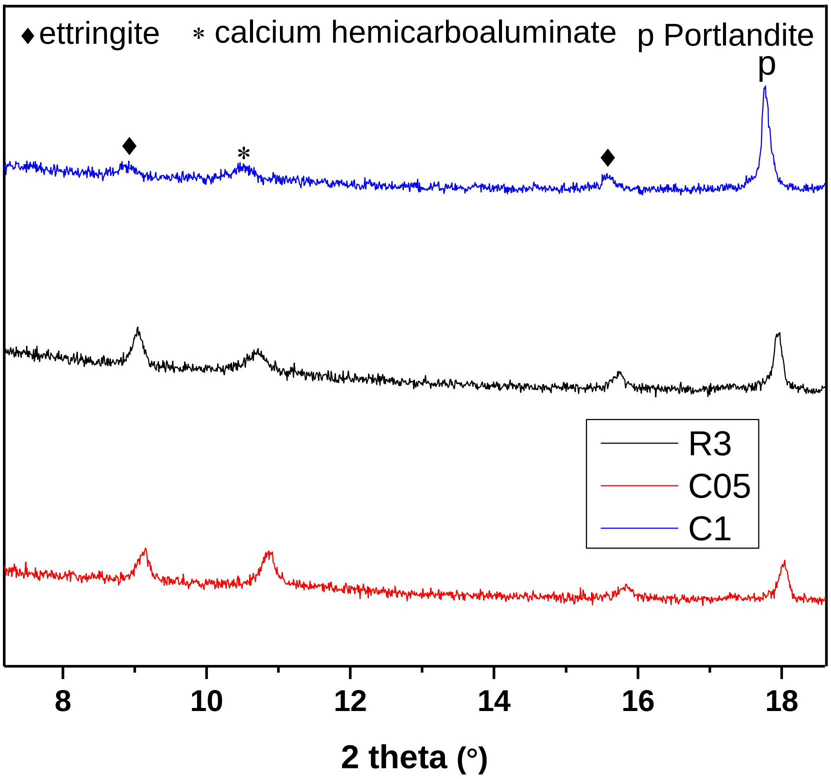

Figure 9: X ray diffraction spectrum comparing mixes R3, C05 and C1 at 28 days.

Changes in the hydration phases formed did not only happen with increased amounts of citric or lactic acid but also with age. Mix C05 displayed the highest peaks of ettringite formation as seen from Figure.10. This increased hydrate formation did reflect in the mechanical strength results and it can be observed that at day 14, the compressive strength reached nearly that of the reference mix without citric acid, R3. Furthermore, it can be seen from Figure.10 that mix C05 experiences significant reductions in ettringite and portlandite going from 14 days to 28 days.

These results support the mechanical strength results from Figures. 3 and 4 which also show a reduction in compressive strength from 14 to 28 days.

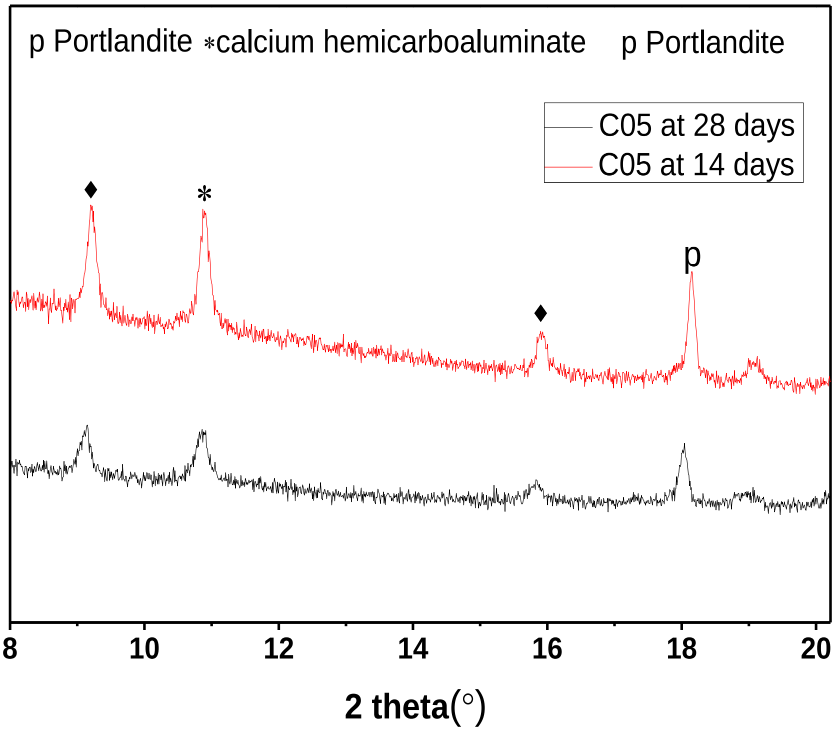

Figure 10: X ray diffraction spectrum comparing mix C05 at 14 and 28 days.

4 Conclusion

This research intended to uncover how citric and lactic acids, both carboxylic acids, affect the strength development of PC/CAC blended cementitious binders at early ages. These preliminary results show that organic admixtures, in this case of citric acid, has not been effective at significantly increasing the ettringite formation but in fact in higher concentrations, adversely affected strength development and precipitation of C-S-H. These results however should not rule out the investigation of other carboxylic acids which may, in varying quantities, assist in the hydration of PC/CAC systems.

- The compressive and flexural strength of PC/CAC blended cement was greatly reduced by the addition of citric acid. Addition of citric acid at 1% wt. lead to an increase in Portlandite but at higher concentrations blocked the dissolution of cement hydrates. From the three concentrations of citric acid tested, 1% wt. addition was the only concentration that did not cause a reduction in strength going from 14 to 28 days. Based on these findings, water reducers containing citric acid would not be recommended for use with PC/CAC blended cementitious materials.
- The addition of lactic acid in smaller amounts (0.5 and 1%) increases the compressive strength by almost 20% for 7 and 14 days but left the 28-day compressive strength unaffected and the 28-day flexural strength of PC/CAC blended cement was not exceeded by the addition of lactic acid. However with lactic acid, a reduction in Portlandite formation was observed at 3% addition. Also observed was that an increase in portlandite is coupled with a decrease in ettringite formation for mixes with increasing additions of lactic acid. Lactic acid shows positive signs of strength enhancement at early stages and in low concentrations i.e. 0.5 and 1% wt., but in higher concentrations i.e. 3% wt. is responsible for initiating the consumption of Portlandite in PC/CAC binders.
- Contrary to the results of another study, citric acid is responsible for reducing the amount of strength inducing hydrates in PC/CAC binders, but also blocks the dissolution of existing cement grains up to 28 days. Also the main long term strength contributing hydrate, C-S-H, remained undetected

for mixes with either lactic acid or citric acid at early ages up to 28 days through SEM/XRD analysis.

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